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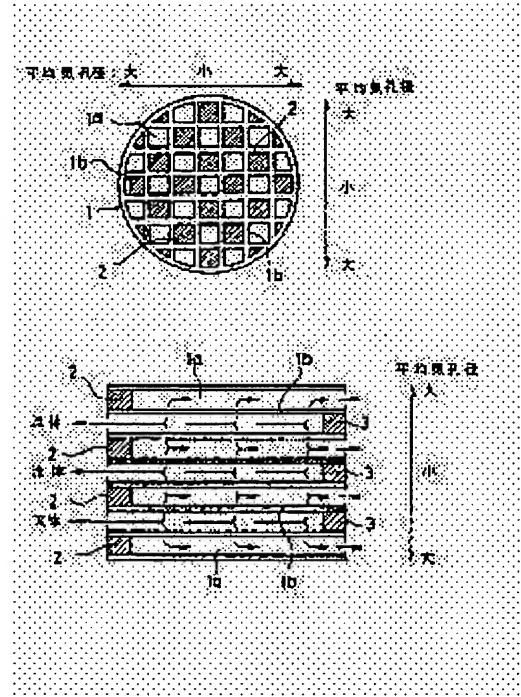
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## (54) SILICON CARBIDE HONEYCOMB STRUCTURE AND PRODUCTION THEREOF

(57)Abstract:

PURPOSE: To obtain the title honeycomb structure freed from developing melt damage or thermal shock fracture when heated for the purpose of its reuse, by forming partition walls made of porous material having three-dimensional network structure, and also forming the mean size of the open pores in said network structure so as to become gradually larger from the partition walls located at the center of the structure towards those walls located on the periphery.

CONSTITUTION: The objective silicon carbide honeycomb structure in which numerous penetrating holes 1a are arranged side by side in the axis direction through thin partition walls 1b. The constitution of this honeycomb structure is as follows: the partition walls 1b are made of a porous material having three-dimensional network structure composed mainly of lamellar crystals with an average aspect ratio of 2W50, and the average size of the open pores in said network structure is formed so as to become stepwise or continuously larger from the partition walls located at the center of the structure towards those walls located on the periphery (in the direction expressed by the arrow).



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⑮ 発明の名称 炭化ケイ素質ハニカム構造体及びその製造方法

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## 明細書

## 1. 発明の名称

炭化ケイ素質ハニカム構造体及びその製造方法

## 2. 特許請求の範囲

(1) 薄い隔壁を隔てて軸方向に多数の貫通孔が隣接している炭化ケイ素質ハニカム構造体において、該隔壁が、平均アスペクト比2~50の範囲内の板状結晶を主体として構成される三次元の網目構造を有する多孔質体からなり、かつ、前記網目構造の開放気孔の平均気孔径が、ハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように形成されていことを特徴とする炭化ケイ素質ハニカム構造体。

(2) 前記板状結晶の平均短軸方向の厚みが1~500μmである特許請求の範囲第1項記載の炭化ケイ素質ハニカム構造体。

(3) 前記板状結晶が前記多孔質体100重量部に対し、少なくとも20重量部含まれている特許

請求の範囲第1項または第2項記載の炭化ケイ素質ハニカム構造体。

(4) 前記三次元網目構造の開放気孔の平均気孔径が1~5.0μmの範囲である特許請求の範囲第1項~第3項いずれか1項に記載の炭化ケイ素質ハニカム構造体。

(5) 前記三次元の網目構造開放気孔率が20~95容量%である特許請求の範囲第1項~第4項いずれか1項に記載の炭化ケイ素質ハニカム構造体。

(6) 前記炭化ケイ素質多孔質体の比表面積が少なくとも0.05m<sup>2</sup>/gである特許請求の範囲第1項~第5項いずれか1項に記載の炭化ケイ素質ハニカム構造体。

(7) 炭化ケイ素粉末を出発原料とし必要により結晶成長助剤を添加し混合物を得る第一工程:

該混合物に成形用結合剤を添加しハニカム状に成形した成形体を得る第二工程:

該成形体を耐熱性の容器内に挿入して外気の侵入を遮断しつつ2000~2500°Cの温度範囲

内で焼成する第三工程；

とからなる隔壁に三次元網目構造の開放気孔を有する炭化ケイ素質ハニカム構造体の製造方法において、

前記第二工程における成形体を得るに際し、アルミニウム、ホウ素、カルシウム、クロム、鉄、ランタン、リチウム、イットリウム、珪素、窒素、酸素、炭素の中から選ばれる少なくとも一種の元素又はそれらの化合物を成形体内に濃度勾配が生じるように存在せしめ、前記網目構造の開放気孔の平均気孔径がハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように成形することを特徴とする炭化ケイ素質ハニカム構造体の製造方法。

### 3. 発明の詳細な説明

#### 【発明の目的】

#### （産業上の利用分野）

本発明は炭化ケイ素質ハニカム構造体及びその製造方法に関し、更に詳しくは、ハニカム構造体の隔壁表面で生じる熱移動、化学反応、物質移動

また、セラミック粒子が板状で表面が比較的平滑であるために、粒体物の接触面積が少なく、上記した熱移動等を効率よく行なうことができないという問題がある。

一方、炭化ケイ素を主成分とするものは、隔壁中に存在する気孔の占める割合が30～40%と比較的少ないため、通気抵抗が大きくなり気体や液体の粒体物との接触有効面積が少ないので触媒担体やフィルターなどの用途には適さないものが多いという問題がある。

本発明者は、このような問題を解決するハニカム構造体として、先に、板状結晶が多方向に複雑な状態で絡み合い三次元の網目構造が形成され、気孔部の占める割合が比較的高い炭化ケイ素質多孔質隔壁を有するハニカム構造体を特願昭59-143235号として提案している。

#### （発明が解決しようとする問題点）

このハニカム構造体は、従来のものに比し、有効比表面積が大きくハニカムの軸方向の流れから流体を積極的に多孔質内に取り込み易く、しか

等を効率よく行なうことができ、さらに再使用時の加熱によるハニカム構造体の溶損あるいは熱衝撃破壊を防ぐことができる炭化ケイ素質ハニカム構造体及びその製造方法に関する。

#### （従来の技術）

例えば第1図、第2図に示すような薄い隔壁1bを介して蜂の巣状に連なる無数の貫通孔の一方の端面を例えれば縦横一つおきに封止材2を充填し封止し、この封止した貫通孔に隣接している貫通孔の他端面に封止材3を充填し封止した多孔質隔壁からなるセラミック質のハニカム構造体は、自動車のディーゼルエンジンを始めとして各種燃焼機器の排ガス中に含まれる微粒炭素を吸着して浄化する排ガス浄化装置として知られている。

かかるハニカム構造体には、従来、コージェライトや炭化ケイ素質を主成分とするものが多く用いられているが、コージェライトを主成分とするものにあっては、押出し成形される際に隔壁のセラミック粒子が押出し方向に配向し易いため、流体物が隔壁を通過し難く圧力損失が大きくなり、

も、隔壁表面で生じる流体の流れが乱流となるため、流れ内における拡散、攪拌等による均一化が促進され、隔壁表面に生じる熱移動、化学反応、物質移動等を有効に行なわしめるという効果がある。また、炭化ケイ素を主成分としているため、コージェライトを主成分とするものよりも融点が高く再使用時の加熱の際に高温に耐え得るという特性もある。

しかしながら、かかる場合、すなわちハニカム構造体を再使用する目的で隔壁上に吸着、回収された微粒炭素をバーナーあるいはヒーターによって加熱した場合、回収された炭素自身の燃焼熱が往々として中央部分に蓄積し易く、炭化ケイ素を主成分とするとはいえ該部分の貫通孔を形成している薄い隔壁を溶損あるいは熱衝撃破壊させ、その後の使用を不能にする場合があるという問題がある。

本発明は、上記した炭化ケイ素質ハニカム構造体の効果を減少せしめることなく、再使用を目的とする加熱に対しても溶損あるいは熱衝撃破壊す

る虞れのない新規な炭化ケイ素質ハニカム構造体及びその製造方法を提供することを目的とする。

#### 【発明の構成】

##### (問題点を解決するための手段)

本発明の炭化ケイ素質ハニカム構造体は、薄い隔壁を隔てて軸方向に多数の貫通孔が隣接している炭化ケイ素質ハニカム構造体において、該隔壁が、平均アスペクト比2~50の範囲内の板状結晶を主体として構成される三次元の網目構造を有する多孔質体からなり、かつ、前記網目構造の開放気孔の平均気孔径が、ハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように形成されていることを特徴とする。

隔壁において、板状結晶が複雑な状態で絡み合い三次元の網目構造が形成されるのは、焼結を後述する所定の条件下で進行せしめるためである。

平均アスペクト比を2~50としたのは、2未

数が少なく接合強度が小さくなり、その結果、保形し難くなるためである。

そして、前記板状結晶は前記多孔質体100重量部に対し、少なくとも20重量部を占めることができが好ましい。20重量部未満の場合には結晶によって形成される気孔が、結晶の占める容量に対して少なくなり、前記熱移動、化学反応あるいは物質移動の行なわれる有効面積が少なくなる。また、板状結晶の接合面積が少なくなるため、多孔質体自体の機械的強度が著しく低下するからである。なかでも、少なくとも40重量部であることが最も好ましい。

本発明の炭化ケイ素質ハニカム構造体は、上記した三次元の網目構造を有する多孔質体から成る隔壁を有し、さらに、前記網目構造の開放気孔の平均気孔径がハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように形成されていることを特徴とする。

その理由は、上記したように、ハニカム構造体

の場合には、炭化ケイ素結晶によって構成される気孔が、結晶の占める容積に比べて小さくなり、高い気孔率と大きな気孔径を有することが困難となるためである。一方、50を超えた場合には、板状結晶の接合部の強度が低くなるため、多孔質体自体の強度が著しく低いものとなり、その結果、ハニカム構造体の保形をも困難にするからである。より好ましいアスペクト比は3~30の範囲である。

なお、ここでいう炭化ケイ素質板状結晶のアスペクト比(R)は焼結体の任意の断面において観察される個々の板状結晶の最大長さ(X)と平均短軸方向の厚み(Y)との比であり、すなわち、 $R = X / Y$ で表わされる値である。

また、板状結晶の平均短軸方向の厚みは1~500μであることが好ましく、なかでも3~300μであることがより好ましい。その理由は、1μより小さいと前記板状結晶により形成される気孔が小さくなり流量が小さくなるためであり、500μよりも大きいと板状結晶の接合部の

を構成する多孔質体よりなる隔壁の平均気孔径が構造体全部に亘り均一のものにあっては再使用する際の燃焼熱が中央部に蓄積し易いのに対し、本発明の如く、中央部から外周部に向かうにつれ平均気孔径を大きくしたものは、かかる燃焼熱が中央部に留まることなく外周部に円滑に放散されるため、再使用の際の加熱に伴なう隔壁の溶損あるいは熱衝撃破壊を防ぐことができるからである。

前記網目構造の気孔の平均気孔径は、1~50μの範囲内であることが好ましい。1μ未満の場合には、流体の通過抵抗が小さくなり、一方、50μを超える場合には多孔質体自体の強度が低くなるからである。好ましくは2~30μの範囲である。なお、前記平均気孔径の値は、水銀圧入法により得られる値である。

したがって、本発明のハニカム構造体の隔壁を構成している多孔質体の平均気孔径は、上記した範囲内で、第1図及び第2図矢線で示すように、ハニカム構造体の中央部を最小とし、外周部に向

かうにつれ段階的又は連続的に大きくなっている。

また、前記網目構造の開放気孔率は20~95容量%であることが好ましい。これは、20容量%よりも小さい場合には、気孔の一部が独立気孔化し、前記有効表面積が小さくなるためであり、95容量%よりも大きいと、有効表面積は大きくなるが、ハニカム構造体の保形性が保てなくなるためである。なかでも30~90容量%であることがより好ましい。

さらに、前記炭化ケイ素質隔壁の比表面積が少なくとも0.05m<sup>2</sup>/gであることが好ましく、さらには、0.2m<sup>2</sup>/gであることが最も好ましい。ここで比表面積は空素吸収によるBET法によって求められる値である。

次に本発明の炭化ケイ素質ハニカム構造体の製造方法について説明する。

本発明の炭化ケイ素質ハニカム構造体の製造方法は、炭化ケイ素粉末を出発原料とし必要により結晶成長助剤を添加し混合物を得る第一工程；

結晶であり、焼結に際し、その一部が4H、6Hあるいは15R型等の高温安定型の $\alpha$ 型結晶に相転移して板状結晶を形成し易く、しかも結晶の成長性にも優れているからである。特に60重量%以上が $\beta$ 型炭化ケイ素からなる出発原料を用いることにより本発明の目的とする多孔質体を容易に製造することができる。なかでも、70重量%以上の $\beta$ 型炭化ケイ素を含有する出発原料を使用することが有利である。

結晶成長助剤としては、例えば、アルミニウム、ホウ素、鉄、炭素等が挙げられる。

次に、第二工程において、第一工程において得られた混合物にメチルセルロース、ポリビニルアルコール、水ガラス等の成形用結合剤を添加し、押出し成形、シート成形、プレス成形等の方法によりハニカム状の成形体を得る。そして、アルミニウム、ホウ素、カルシウム、クロム、鉄、ランタン、リチウム、イットリウム、珪素、空素、酸素、炭素の中から選ばれる少なくとも一種の元素又はそれらの化合物を成形体内に濃度勾配が生じ

該混合物に成形用結合剤を添加しハニカム状に成形した成形体を得る第二工程；該成形体を耐熱性の容器内に挿入して外気の侵入を遮断しつつ2000~2500℃の温度範囲内で焼成する第三工程；とからなる隔壁に三次元網目構造の開放気孔を有する炭化ケイ素質ハニカム構造体の製造方法において、前記第二工程における成形体を得るに際し、アルミニウム、ホウ素、カルシウム、クロム、鉄、ランタン、リチウム、イットリウム、珪素、空素、酸素、炭素の中から選ばれる少なくとも一種の元素又はそれらの化合物（以下、場合により単に「遷移層形成助剤」と称す。）を成形体内に濃度勾配が生じるように存在せしめ、前記網目構造の開放気孔の平均気孔径がハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように形成することを特徴とする。

まず、第一工程において、炭化ケイ素粉末を出発原料とすることが好ましい理由は、 $\beta$ 型の炭化ケイ素結晶は比較的低温で合成される低温安定型

るよう存在させる。その方法は、前記成形体に直接前記化合物を含有した溶液を塗布したり、前記成形体の成形用結合剤を除去し多孔質とした後、同様に含浸したりする方法で行なう。

濃度勾配が生じるのは、上記した物質のうち、アルミニウム、ホウ素、カルシウム、クロム、鉄、ランタン、リチウム、イットリウムは、炭化ケイ素の結晶粒成長の速度を速くする働きを有しており、これらの物質の存在する箇所では極めて多くの板状結晶の核が生成され、各々の部分で板状結晶の発達が起こる結果、形成される板状結晶の大きさが制限され、これらの物質が多く存在する箇所ほど細かい組織の三次元網目構造となすことができるからである。

これに対し、珪素、空素、酸素、炭素は上記物質とは逆に炭化ケイ素の結晶粒成長の速度を遅くする働きを有しており、これらの物質の存在する箇所では板状結晶の核生成が抑制され、形成される板状結晶の数が相対的に少なくなる結果、それぞれの板状結晶が比較的大きく成長するため、こ

これらの物質が多く存在する箇所ほど大きな組織の三次元網目構造となすことができるからである。

したがって、網目構造の開放気孔の平均気孔径がハニカム構造体中央部隔壁から外周部隔壁に向かうにつれ、段階的又は連続的に大きくなるように形成された炭化ケイ素質ハニカム構造体を得るために、上記遷移層形成助剤のうち、アルミニウム、ホウ素、カルシウム、クロム、鉄、ランタン、リチウム、イットリウムをハニカム成形体中央部付近に含有させて後述する方法により焼結する方法、あるいは、珪素、窒素、酸素、炭素をハニカム成形体の外周部付近に含有させて後述する方法により焼結する方法、さらには、両方法を併用する方法が挙げられる。

なお、前記遷移層形成助剤は、焼結体中に多量に残存すると炭化ケイ素本来の特性が失われるため、なるべく少いことが望ましく焼結体中におけるその残存量は炭化ケイ素100重量部に対し10重量部以下であることが好ましく、なかでも

素、炭化タンクスステン、モリブデン、炭化モリブデンのうち少なくとも1種以上の材質からなる耐熱性容器を使用することが好ましい。

また、焼成温度を2000～2500℃とするのは、2000℃より低い場合には粒子の成長が不十分で、隔壁を高い強度を有する多孔質体とすることが困難なためであり、2500℃よりも高い場合には炭化ケイ素の昇華が盛んになり、発達した板状結晶が逆にやせ細ってしまい、その結果高い強度を有する多孔質体を得ることが困難となるためである。より好ましくは2100～2300℃の範囲内である。

#### 【実施例】

##### 実施例1

出発原料として使用した炭化ケイ素微粉末は、80重量%が $\beta$ 型結晶からなるものを用いた。この出発原料には不純物としてBが0.01、Cが0.5、A<sub>1</sub>が0.01、Nが0.2、Feが0.08原子量部、その他の元素は痕跡量含まれており、これらの不純物総量は0.81原子量部

5重量部以下であることがより好ましい。

次に、第三工程として、得られた成形体を耐熱性の容器内に封入し、外気の侵入を遮断しつつ2000～2500℃の温度範囲内で焼成する。

耐熱性の容器内に封入し、外気の侵入を遮断しつつ焼成を行なう理由は、隣接する炭化ケイ素結晶同士を融合させ、かつ、板状結晶の成長を促進させることができ、板状結晶が複雑な状態で絡み合い三次元の網目構造が形成されるからである。

なお、板状結晶の成長を促進させることができるのは、炭化ケイ素粒子間における炭化ケイ素の蒸発-再凝聚および/または表面拡散による移動を促進することができるためと考えられる。

これに対し、従来知られている常圧焼結、雰囲気加圧焼結あるいは減圧下における焼結法を試みたところ、板状結晶の成長が困難であるばかりか炭化ケイ素粒子の接合部がネック状にくびれた形状となり、焼結体の強度が低くなつた。

前記耐熱性の容器としては、黒鉛、炭化ケイ

であった。また、この出発原料の平均粒径は0.3mm、比表面積は18.7m<sup>2</sup>/gであった。

この出発原料に成形用結合剤としてメチルセルロースを10重量部、水分を20重量部添加した。これを混練して、押出し成形法により直径13.0mm、長さ120mm、貫通孔の隔壁の厚さ0.3mm、1平方インチ当りの貫通孔数約200の炭化ケイ素質ハニカム成形体を得た。

この成形体を1℃/分の昇温速度で500℃まで酸化雰囲気中で加熱して、前記有機結合剤を酸化除去した。次いで成形体の外周部から20mmの部分に40%のフェノールレジン、アルコール溶液を含浸させ、その後乾燥させた。この結果、外周部より20mmの部分では遊離炭素は8%含まれ内側に向かうにつれて連続的に徐々に減少し中央部より20mmの部分では遊離炭素は0.3%含まれていた。

その後、この成形体を気孔率20%の黒鉛ルーブに入れ、1気圧のアーガス雰囲気中で焼成し

た。

焼成は、 $2^{\circ}\text{C}/\text{分}$ で $2150^{\circ}\text{C}$ まで昇温し、最高温度で4時間保持した。

実施例2～5、比較例1～4

実施例1と同様であるが、フェノールレジンの添加に加えて、中央部より $20\text{mm}$ 径の間にアルミニウム(0.05μ粒子)水溶液を添加し、Aの含有量を0.2重量%とした場合(実施例2)、フェノールレジンの添加を行なわずにBN微粉末(粒径0.2μ)を中心部より $20\text{mm}$ 径の間に塗布し、Bの含有量を0.1重量%とした場合(実施例3)、実施例1と同様であるがフェノールレジンの添加を行なわなかつた場合(比較例1)、全体にBを0.4重量%添加した場合(比較例2)、実施例1と同様であるが焼成温度を $2300^{\circ}\text{C}$ の最高温度での保持時間を10時間とした場合(実施例4)、焼成温度を $2050^{\circ}\text{C}$ の最高温度での保持時間を2時間とした場合(実施例5)、焼成温度を $1800^{\circ}\text{C}$ とした場合(比較例3)、焼成温度を $2550^{\circ}\text{C}$ とした場合(比

較例4)のハニカム構造体の隔壁構造、性能等の結果を次表に示す。なお、表中aはハニカム構造体の中央部附近に位置する隔壁の、bはその外周部に位置する隔壁の、cはさらにその外周部に位置する隔壁を示す。

表

|     |                     | ハニカム成形体中の添加物 |           |                    | ハニカム成形体の焼成条件 |          |          | ハニカム構造体隔壁構造 |               |                    |                |            | 性能                     |                   |                  |
|-----|---------------------|--------------|-----------|--------------------|--------------|----------|----------|-------------|---------------|--------------------|----------------|------------|------------------------|-------------------|------------------|
|     |                     | 添加物          | 外周部含有量(%) | 中央部含有量(%)          | 使用アルツボ       | 焼成温度(°C) | 保持時間(hr) | 位置          | 板上結晶の平均アスペクト比 | 板上結晶の平均粒度方向の厚み(μm) | 開放気孔の平均気孔径(μm) | 開放気孔率(%TD) | アスペクト比2～50の板上結晶の含有率(%) | 抽抜粒子たい積厚み(mm/5hr) | 燃焼除去時のハニカム温度(°C) |
| 実施例 | 1<br>遊離<br>炭素       | 8            | 0.3       | 気孔率<br>20%<br>アルツボ | 2150         | 4        |          | a           | 4             | 20                 | 8              | 46         | 80                     | 0.4               | 1020             |
|     |                     |              |           |                    |              |          |          | b           | 3.5           | 28                 | 12             | 48         | 83                     | 0.5               | 1010             |
|     |                     |              |           |                    |              |          |          | c           | 3.2           | 43                 | 15             | 45         | 85                     | 0.6               | 1000             |
|     | 2<br>遊離<br>炭素<br>A2 | 8            | 0.3       | 気孔率<br>20%<br>アルツボ | 2150         | 4        |          | a           | 6             | 4                  | 3              | 42         | 95                     | 0.3               | 1060             |
|     |                     |              |           |                    |              |          |          | b           | 4             | 13                 | 8              | 43         | 90                     | 0.5               | 1080             |
|     |                     |              |           |                    |              |          |          | c           | 3.4           | 40                 | 14             | 44         | 87                     | 0.8               | 1100             |
|     | 3<br>遊離<br>炭素       | 8            | 0.01      | 0.1                | 〃            | 2150     | 4        | a           | 8             | 3                  | 4              | 40         | 98                     | 0.5               | 1100             |
|     |                     |              |           |                    |              |          |          | b           | 6             | 12                 | 8              | 40         | 98                     | 0.8               | 1140             |
|     |                     |              |           |                    |              |          |          | c           | 4             | 26                 | 12             | 42         | 92                     | 0.8               | 1150             |
|     | 4<br>遊離<br>炭素       | 8            | 0.3       | 〃                  | 2300         | 10       |          | a           | 3.8           | 43                 | 13             | 48         | 92                     | 0.4               | 1000             |
|     |                     |              |           |                    |              |          |          | b           | 3.1           | 55                 | 21             | 47         | 90                     | 0.5               | 1000             |
|     |                     |              |           |                    |              |          |          | c           | 2.5           | 62                 | 28             | 47         | 90                     | 0.7               | 980              |
|     | 5<br>遊離<br>炭素       | 8            | 0.3       | 〃                  | 2050         | 2        |          | a           | 4.2           | 11                 | 5              | 46         | 63                     | 0.5               | 1050             |
|     |                     |              |           |                    |              |          |          | b           | 3.5           | 18                 | 8              | 48         | 60                     | 0.6               | 1060             |
|     |                     |              |           |                    |              |          |          | c           | 2.5           | 22                 | 8              | 46         | 55                     | 0.8               | 1080             |

(表の続き)

|     | ハニカム成形体中の添加物  |           |           | ハニカム成形体の焼成条件 |          |          | ハニカム構造体隔壁構造 |               |                  |                |            |                        | 性能                |                  |
|-----|---------------|-----------|-----------|--------------|----------|----------|-------------|---------------|------------------|----------------|------------|------------------------|-------------------|------------------|
|     | 添加物           | 外周部含有量(%) | 中央部含有量(%) | 使用ルーツ        | 焼成温度(°C) | 保持時間(hr) | 位置          | 板上結晶の平均アスペクト比 | 板上結晶の平均粒径の厚み(μm) | 開放気孔の平均気孔径(μm) | 開放気孔率(ZTD) | アスペクト比2~50の板上結晶の含有率(%) | 抽殻粒子たい積厚み(mm/5hr) | 燃焼除去時のハニカム温度(°C) |
| 比較例 | 1<br>遊離<br>炭素 | 0.3       | 0.3       | 〃            | 2150     | 4        | a           | 3.3           | 44               | 18             | 45         | 83                     | 0.5               | 1150             |
|     |               |           |           |              |          |          | b           | 3.3           | 44               | 18             | 45         | 83                     | 0.5               | 1080             |
|     |               |           |           |              |          |          | c           | 3.3           | 44               | 18             | 45         | 83                     | 0.5               | 950              |
|     | 2<br>8        | 0.4       | 0.4       | 〃            | 2150     | 4        | a           | 7.5           | 2.3              | 5              | 33         | 98                     | 0.8               | 1350             |
|     |               |           |           |              |          |          | b           | 7.5           | 2.3              | 5              | 33         | 96                     | 0.8               | 1200             |
|     |               |           |           |              |          |          | c           | 7.5           | 2.3              | 5              | 33         | 98                     | 0.8               | 1060             |
|     | 3<br>遊離<br>炭素 | 8         | 0.3       | 〃            | 1800     | 4        | a           | 1.1           | 2.3              | 4.2            | 44         | 10                     | 0.8               | 1480             |
|     |               |           |           |              |          |          | b           | 1.2           | 2.2              | 4.5            | 44         | 11                     | 0.8               | 1330             |
|     |               |           |           |              |          |          | c           | 1.0           | 2.5              | 3.8            | 44         | 6                      | 0.8               | 1100             |
|     | 4<br>遊離<br>炭素 | 8         | 0.3       | 〃            | 2550     | 4        | a           | 1.5           | 81               | 45             | 52         | 33                     | 破損                | —                |
|     |               |           |           |              |          |          | b           | 2.1           | 55               | 38             | 53         | 35                     |                   | —                |
|     |               |           |           |              |          |          | c           | 2.5           | 34               | 32             | 54         | 38                     |                   | —                |

表より明らかなように本発明のハニカム構造体は、その中央部の隔壁から外周部の隔壁に向かうにしたがい次第に平均気孔径が大きくなっています。しかも、この構造体を1~30μmの粒子径を有するディーゼルエンジンのバティキュレートトラップフィルターとして使用し排ガス中の微粒子を5時間捕集したところ、積層した微粒子の厚みは、例えば実施例1では、中央部(a)で0.4mm、最外周部(c)では0.6mmといったよう微粒子に、各実施例とも中央部から外周部に向かうにつれてその厚みは連続的に変化した状態となつた。

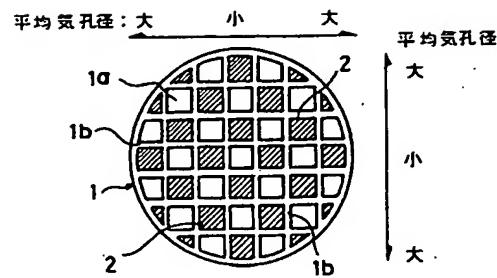
したがって、本発明に係るハニカム構造体に過剰のO<sub>2</sub>を加え、800°Cで着火させたところ、例えば、実施例1では外周部の昇温時の温度は1000°C、中央部の昇温時の温度は1020°Cといったように、各実施例とも極めて温度差が小さく、溶損もなく耐熱衝撃にも全く問題はなかった。

## 【発明の効果】

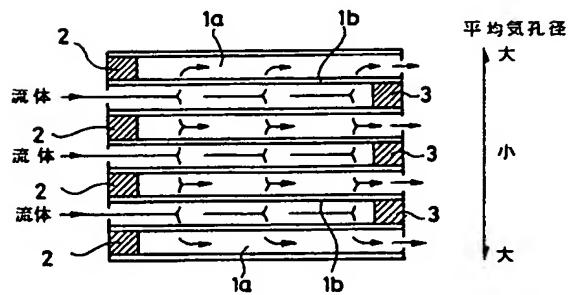
本発明の炭化ケイ素質ハニカム構造体によれば、板状結晶が複雑に絡み合った三次元網目構造を有しているので、隔壁表面に生じる熱移動、化学反応、物質移動等が有効に行なわれるほか、構造体の中央部隔壁から外周部隔壁に向かうに従い平均気孔径が大きくなっているため、再使用する目的で加熱した場合であっても、燃焼熱が中央部に蓄積するようなことがなく隔壁の溶損や熱衝撃破壊を防ぐことができる。

## 4. 図面の簡単な説明

第1図は、本発明のハニカム構造体の平面図であり、第2図は、その縦断面模式図である。



第 1 図



第 2 図

PTO 05-6226

Japanese Kokai Patent Application  
No. Hei 1[1989]-145377

SILICON CARBIDE HONEYCOMB-STRUCTURE AND MANUFACTURE OF SAME

Kiyotaka Tsukada

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SILICON CARBIDE HONEYCOMB-STRUCTURE AND MANUFACTURE OF THE SAME

[Tankakeisoshitsu hanikamukouzoutai oyobi sono seizouhouhou]

Inventor:

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Applicant:

Ibiden Co., Ltd.

[There are no amendments to this patent.]

Claims

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1. A silicon carbide honeycomb structure in which a plurality of passage holes running in the axial direction are adjacent to each other separated by thin barrier walls, said silicon carbide honeycomb structure characterized in that said barrier walls are composed of a porous body having a three-dimensional network structure that has tabular crystals as the primary component with an average aspect ratio in the range of 2 to 50, and is formed so that the average pore diameter of the open pores in said network structure increases in a step-wise or continuous manner from the central barrier walls to the circumferential barrier walls in the honeycomb structure.

2. The silicon carbide honeycomb structure according to Claim 1, wherein the average thickness in the direction of the minor diameter of said tabular crystals is 1 to 500  $\mu\text{m}$ .

3. The silicon carbide honeycomb structure according to Claim 1 or 2, wherein said tabular crystals are contained at 20 parts by weight or more with respect to 100 parts by weight of said porous body.

4. The silicon carbide honeycomb structure according to any of Claims 1 to 3, wherein the average pore diameter of the open pores in said three-dimensional network structure is in the range of 1 to 50  $\mu\text{m}$ .

5. The silicon carbide honeycomb structure according to any of Claims 1 to 4, wherein the open porosity in said three-dimensional network structure is 20 to 95 vol%.

6. The silicon carbide honeycomb structure according to any of Claims 1 to 5, wherein the specific surface area of said silicon carbide porous body is at least 0.05  $\text{m}^2/\text{g}$ .

7. A method for producing a silicon carbide honeycomb structure where the barrier walls have open pores with a three-dimensional network structure, which comprises a first step in which silicon carbide powder is used as starting material and a mixture is obtained by adding crystal growth aid as necessary; a second step in which binder for molding is added to said mixture, and a molded body is obtained that has been molded into a honeycomb form; and a third step in which said molded body is placed in a heat-resistant container and is fired in the temperature range of 2000 to 2500°C while blocking the ingress of external air, said method for producing a silicon carbide honeycomb structure characterized in that, in obtaining the molded body in the second step above, at least one element, or compound thereof, selected from aluminum, boron, calcium, chrome, iron, lanthanum, lithium, yttrium, silicon, nitrogen, oxygen and carbon is introduced so that a concentration gradient is produced in the molded body, and molding is carried out so that the average pore diameter of the open pores in said network

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\* Numbers in the right margin indicate pagination of the original text.

structure increases in a step-wise or continuous manner from the central barrier walls to the peripheral barrier walls of the honeycomb structure.

### Detailed description of the invention

#### Industrial application field

The present invention relates to a silicon carbide honeycomb structure and a method for its production. In additional detail, the present invention relates to a silicon carbide honeycomb structure and a method for its production, whereby it is possible to efficiently perform heat transfer, chemical reactions, material transfer and the like at the barrier wall surfaces of the honeycomb structure, and whereby fusion damage or thermal shock damage to the honeycomb structure can be prevented when heating is performed for reuse.

#### Prior art

As shown in Figure 1 and Figure 2, for example, ceramic honeycomb structures are known which comprise porous barrier walls in which one end of numerous passage holes that are connected in the form of a beehive via thin barrier walls (1b) are filled and sealed with packing (2), for example, every other hole both vertically and horizontally, whereas the other ends of the passage holes adjacent to the sealed passage holes are filled with sealing material (3) and sealed. These structures are known as exhaust gas cleaners that adsorb and remove microparticulate carbon contained in exhaust gas from various types of combustion devices such as diesel automobile engines.

In the past, cordierite and silicon carbide have frequently been used as primary components in these types of honeycomb structures, but when cordierite is used as the primary component, the ceramic particles of the barrier walls tend to orient in the direction of extrusion during extrusion molding, which makes it difficult for fluids to pass through the barrier walls, and increases pressure loss. In addition, ceramic particles have small contact surface areas because they are tabular and have comparatively smooth surfaces, which leads to problems with efficient performance of thermal transfer and the other operations indicated above.

When silicon carbide is used as the primary component, on the other hand, the ratio of pores present in the barrier walls is comparatively low, at 30 to 40%, and so the air flow resistance increases and the utilized contact surface area between the gas or liquid and the particles decreases. Consequently, there is the problem that such materials are not suitable for applications such as catalyst carriers and filters.

The inventor of the present invention has previously offered a honeycomb structure that solves these types of problems in Japanese Patent Application No. Sho 59[1984]-143235, where the honeycomb structure has silicon carbide porous barrier walls that are constituted by a

comparatively high ratio of pores and a three-dimensional network structure is formed in which platelet-form crystals are intertwined in a complicated multidirectional manner.

#### Problems to be solved by the invention

Due to its large effective specific surface areas, this honeycomb structure, in comparison to conventional materials, facilitates active incorporation of liquid from a flow that runs in the axial direction of the honeycomb structure, while also causing turbulent flow of liquid generated by the barrier walls, so that uniformity is promoted by diffusion and agitation within the flow. In addition, the honeycomb structure also has the merit of performing effective thermal transfer, chemical reactions, material transfers and other functions at the surfaces of the barrier walls. Because the material has silicon carbide as the primary component, it also has characteristics whereby the melting point is higher than materials in which cordierite is the primary component, and the material can thus withstand high temperatures occurring during heating for reuse.

However, when microparticulate carbon that has been adsorbed and recovered on the barrier walls is heated with a burner or heater with the aim of reusing the honeycomb structure, the heat of combustion of the carbon itself that has been recovered tends to accumulate in the center regions, and so there is the problem that use may be impossible due to fusion damage or thermal shock damage to the thin barrier walls that form the passage holes in this region, even when silicon carbide has been used as the primary component.

The present invention has the objective of offering a novel silicon carbide honeycomb structure and method for its production whereby the effects of the aforementioned silicon carbide honeycomb structure are not compromised and there is no danger of fusion damage or thermal shock damage when the material is heated for reuse. /3

#### Constitution of the invention

#### Means to solve the problems

The silicon carbide honeycomb structure of the present invention is a silicon carbide honeycomb structure in which a plurality of passage holes running in the axial direction are adjacent to each other separated by thin barrier walls, where this silicon carbide honeycomb structure is characterized in that the barrier walls are composed of a porous body having a three-dimensional network structure that has tabular crystals as the primary component with an average aspect ratio in the range of 2 to 50, and is formed so that the average pore diameter of the open pores in the aforementioned network structure increases in a step-wise or continuous manner from the central barrier walls to the circumferential barrier walls in the honeycomb structure.

Formation of a three-dimensional network structure in which tabular crystals are intertwined in a complex form in the barrier walls is performed in order to facilitate sintering under the specified conditions described below.

The reason that the average aspect ratio is 2 to 50 is that the pores that are constituted by the silicon carbide crystals have a comparatively small volumetric ratio of crystals when the [aspect] ratio is less than 2, making it difficult to form large pore diameters with high porosity. If the ratio exceeds 50, on the other hand, then the strength of the joints of the tabular crystals decreases, leading to a dramatic decrease in the strength of the porous body itself. As a result, preserving the shape of the honeycomb structure becomes difficult. A more preferable aspect ratio range is 3 to 30.

The aspect ratio (R) of the silicon carbide tabular crystals referred to herein is the ratio of the maximum length (X) of the individual tabular crystals observed over any cross section of the sintered body and the average thickness (Y) along the minor diameter thereof; specifically, the value expressed as  $R = X/Y$ .

In addition, the average thickness of the tabular crystals in the direction of the minor diameter is preferably 1 to 500  $\mu\text{m}$ , with 3 to 300  $\mu\text{m}$  being additionally desirable. The reason for this is that the resulting pores formed from the above tabular crystals will be small if the thickness is less than 1  $\mu\text{m}$ , and the flow rate will decrease. If the thickness is greater than 500  $\mu\text{m}$ , on the other hand, then the number of joints between tabular crystals will decrease, reducing joint strength, and making shape retention difficult.

The above tabular crystals preferably account for at least 20 parts by weight with respect to 100 parts by weight of the above porous body. If this amount is less than 20 parts by weight, then the pores that are formed by the crystals will be small relative to the volume accounted for by the crystals, which will decrease the effective surface area for performing the thermal transfer, chemical reaction or material transfer function referred to above. In addition, because the joint surface area of the tabular crystals is reduced, there may be a dramatic decrease in the mechanical strength of the porous body itself. It is the most preferable for the amount to be at least 40 parts by weight.

The silicon carbide honeycomb structure of the present invention has barrier walls comprising a porous body having the above three-dimensional network structure and, in addition, is characterized in that the pores are formed so that the average pore diameter of the open pores in the above network structure becomes larger in a step-wise or continuous manner from the central barrier walls to the circumferential barrier walls of the honeycomb structure.

The reason for this, as stated above, is that when the average pore diameter of the barrier walls consisting of porous body that constitutes the honeycomb structure is constant over the entire structure, then the heat of combustion when reuse is intended will tend to accumulate at

the center. With the present invention, on the other hand, the average pore diameter increases from the center to the periphery, so that the heat of combustion does not accumulate in the center regions and is smoothly released outwards, making it possible to prevent fusion damage or thermal shock damage to the barrier walls that occurs in conjunction with heating for reuse.

The average pore diameter of the pores of the above network structure is preferably in the range of 1 to 50  $\mu\text{m}$ . If the diameter is less than 1  $\mu\text{m}$ , then the resistance to passage of liquid will decrease [sic], whereas if this diameter exceeds 50  $\mu\text{m}$ , then the strength of the porous body itself will decrease. A preferred range is 2 to 30  $\mu\text{m}$ . The above value of the average pore diameter is a value obtained by the mercury pressure method.

Consequently, the average pore diameter of the porous body that constitutes the barrier walls of the honeycomb structure of the present invention is within the above range and, as indicated by the broken line in Figure 1 and Figure 2, the diameter is the smallest at the center region of the honeycomb structure and increases in a step-wise or continuous manner towards the peripheral regions.

/4

The open porosity of the aforementioned network structure is preferably 20 to 95 vol%. This is because some of the pores will be isolated pores if the porosity is less than 20 vol%, and the aforementioned effective surface area will decrease. If the value exceeds 95 vol%, on the other hand, then the effective surface area will increase, but the capacity for shape retention of the honeycomb structure will be preserved. It is preferable for the value to be 30 to 90 vol%.

In addition, the minimum specific surface area of the aforementioned silicon carbide barrier walls is preferably 0.05  $\text{m}^2/\text{g}$ , with 0.2  $\text{m}^2/\text{g}$  being the most preferred. The specific surface area referred to herein is a value determined by the BET method using nitrogen absorption.

The method for producing the silicon carbide honeycomb structure of the present invention will now be discussed.

The method for producing the silicon carbide honeycomb structure of the present invention is a method for producing a three-dimensional network structure of open pores in the barrier walls, which comprises a first step in which silicon carbide powder is used as starting material and a mixture is obtained by adding crystal growth aid as necessary; a second step in which binder for molding is added to this mixture, and a molded body is obtained by molding the material into a honeycomb form; and a third step in which the molded body is inserted into a heat-resistant container and is fired in the temperature range of 2000 to 2500°C while shielding it from the ingress of external air. This method for producing a silicon carbide honeycomb structure is characterized in that, in order to obtain a molding in the second step above, at least one element or compound thereof selected from aluminum, boron, calcium, chrome, iron, lanthanum, lithium, yttrium, silicon, nitrogen, oxygen and carbon (referred to below as "transfer

layer forming aid") is introduced into the molded body so that a concentration gradient is produced, and thus the average pore diameter of the open pores in the network structure increases in step-wise or continuous manner from the central barrier walls to the peripheral barrier walls of the honeycomb structure.

In the first step, the reason that it is preferable to use silicon carbide powder as the starting material is that  $\beta$ -form silicon carbide crystals are low-temperature stable crystals that are synthesized at comparatively low temperatures. During sintering, some of the crystals undergo a phase transition to high-temperature stable  $\beta$ -crystals such as 4H, 6H or 15R forms, thus facilitating the formation of tabular crystals. In addition, the material has excellent crystal growth properties. In particular, by using a starting material that consists of 60 wt% or greater of  $\beta$ -form silicon carbide, it is possible to produce the porous body that is the objective of the present invention. It is even more advantageous to use as starting material that contains 70 wt% or greater of  $\beta$ -form silicon carbide.

Examples of crystal growth aids that may be cited include aluminum, boron, iron and carbon.

Next, in the second step, a molding binder such as methyl cellulose, polyvinyl alcohol or water glass is added to the mixture obtained in the first step, and a honeycomb-form molded body is obtained by extrusion molding, sheet molding, press molding or other method. Next, at least one element or compound thereof selected from aluminum, boron, calcium, chrome, iron, lanthanum, lithium, yttrium, silicon, nitrogen, oxygen and carbon is introduced so that a concentration gradient is generated in the molded body. This method involves applying a solution containing the above compound directly to the molded body, or removing the molding binder from the molded body to produce a porous condition, followed by infusion in a similar manner.

Formation of a concentration gradient is carried out because aluminum, boron, calcium, chrome, iron, lanthanum, lithium and yttrium among the above substances have a tendency to increase the rate of silicon carbide crystallite growth. Many nuclei of tabular crystals thus are produced in locations in which these substances are present, and tabular crystals are thus generated in the regions. As a result, the size of the tabular crystals that are formed is inhibited, so that a three-dimensional network structure with a finer structure can be produced in regions where a large amount of these substances is present.

Silicon, nitrogen, oxygen and carbon, on the other hand, tend to slow the rate of crystallite growth with silicon carbide, and so nucleation of tabular crystals is inhibited in regions where these substances are present, leading to a comparatively low number of tabular crystals that are formed. As a result, each of the tabular crystals grows to a comparatively large

size, so that a three-dimensional network structure is produced that has more coarse structure in regions in which large quantities of these substances are present.

Consequently, examples of methods that may be used in order to obtain a silicon carbide honeycomb structure in which the average pore diameter of the open pores in the network structure increases in a step-wise or continuous manner from the central barrier walls to the peripheral barrier walls of the honeycomb structure include a method in which aluminum, boron, calcium, chrome, iron, lanthanum, lithium or yttrium transfer layer formation aid is introduced near the center of the honeycomb molded body using the method described below, followed by sintering; a method in which silicon, nitrogen, oxygen or carbon is introduced near the outer periphery of the honeycomb molded body and sintering is carried out by the method described below; or a method in which the two methods are carried out in conjunction.

If the above transfer layer formation aids are present in large amounts in the sintered body, the characteristics of the silicon carbide itself will be lost, and so it is preferable for there to be as little of the material as possible. It is desirable for the residual amount thereof in the sintered body to be 10 parts by weight or less with respect to 100 parts by weight of the silicon carbide, with 5 parts by weight or less being further desirable.

Next, in the third step, the resulting molded body is sealed in a heat-resistant container, and is sintered in a temperature range of 2000 to 2500°C while preventing the ingress of external air.

The reason that the material is placed in a heat-resistant container and is sintered while preventing the ingress of external air is that fusion of adjacent silicon carbide crystals and growth of tabular crystals are thereby promoted, and a three-dimensional network structure is thus produced in which the tabular crystals are intertwined in a complex manner.

Stimulation of the growth of tabular crystals is thought to result from the promotion of evaporation-recondensation of silicon carbide between the silicon carbide particles and/or movement by means of surface diffusion.

In contrast, when a conventional sintering method carried out at normal pressure, at atmospheric pressure, or under reduced pressure is attempted, not only is the growth of tabular crystals poor, but the joints between silicon carbide microparticles assume a constricted form similar to necking, which decreases the strength of the sintered body.

The aforementioned heat resistant container is preferably a heat resistant container that is composed of at least one material selected from graphite, silicon carbide, tungsten carbide, molybdenum and molybdenum carbide.

In addition, the reason that the sintering temperature is 2000 to 2500°C is that particle growth will be insufficient at temperatures below 2000°C and the production of a porous body having high barrier wall strength will be difficult. If the temperature is greater than 2500°C, on the

other hand, evaporation of silicon carbide will be extreme, and the tabular crystals will conversely shrink, making it difficult to produce a porous body having high strength. It is more preferable for the range to be 2100 to 2300°C

### Application examples

#### Application Example 1

The silicon carbide micropowder used as the starting material was a material comprising 80 wt% of  $\beta$ -form crystals. The amounts of impurities contained in the starting material, in terms of parts by atomic weight, were 0.01 of B, 0.5 of C, 0.01 of Al, 0.2 of N and 0.08 of Fe, with other elements being present in trace amounts. The total amount of these impurities was 0.81 parts by atomic weight. In addition, the average particle diameter of the starting material was 0.3  $\mu\text{m}$ , and the specific surface area was  $18.7 \text{ m}^2/\text{g}$ .

10 parts by weight of methylcellulose and 20 parts by weight of water were added as molding binder to the starting material. The materials were then kneaded, and an extrusion molding method was used in order to produce a silicon carbide honeycomb structure with a diameter of 130 mm, a length of 120 mm, a passage hole barrier wall thickness of 0.3 mm and a passage hole number of approximately 200 per square inch.

This molded body was then heated in an oxidative atmosphere to 500°C at a rate of elevation of 1°C/min in order to oxidize and remove the aforementioned organic binder. 40% phenol resin alcohol solution was then infused over a 20 mm region from the periphery of the molded body, and the material was then dried. As a result, the free carbon level was 8% at 20 mm from the outer periphery, and gradually decreased in a continuous manner towards the interior to produce a free carbon content of 0.3% at a location 20 mm from the center.

Subsequently, the molded body was introduced into a graphite crucible with a porosity of 20%, and was sintered in an Ar gas atmosphere at 1 atm.

Sintering was carried out by increasing the temperature to 2150°C at 2°C/min and was retained for 4 h at the maximum temperature.

#### Application Examples 2-5, Comparative Examples 1 to 4

The results regarding barrier wall structure, performance and other aspects of the honeycomb structure are presented in the following table for cases in which the same procedure as in Application Example 1 was carried out, but in addition to the phenol resin, an aqueous solution of alumina sol (0.05  $\mu\text{m}$  particles) was added over a 20 mm diameter region from the center so that the Al content was 0.2 wt% (Application Example 2); or BN micropowder (particle diameter 0.2  $\mu\text{m}$ ) was applied over a 20 mm diameter region from the center without adding phenol resin so that the B content was 0.1 wt% (Application Example 3); or the material was

4225  
314  
16900  
13266.50

16900  
4225  
12675  
13266.50

produced in the same manner as in Application Example 1, but phenol resin was not added (Comparative Example 1); or the overall B content was changed to 0.4 wt% (Comparative Example 2); or the same procedure as in Application Example 1 was carried out but the sintering temperature was a maximum temperature of 2300°C and the residence time was 10 h (Application Example 4); or the sintering temperature was a maximum temperature of 2050°C and the residence time was 2 h (Application Example 5); or the sintering temperature was 1800°C (Comparative Example 3); or the sintering temperature was 2550°C (Comparative Example 4). "a" in the table denotes barrier walls positioned near the center of the honeycomb structure, "b" denotes barrier walls situated at the periphery, and "c" denotes barrier walls situated farther to the periphery.

Table

|              |               | ハニカム成形体中の<br>のはく物 |                  |                          | ハニカム成形体<br>の成形条件 |               |               | ハニカム成形体脱脂精製 |                           |  |                        |               |                                       | 注記                        |                              |
|--------------|---------------|-------------------|------------------|--------------------------|------------------|---------------|---------------|-------------|---------------------------|--|------------------------|---------------|---------------------------------------|---------------------------|------------------------------|
|              |               | 追加<br>熱           | 外筒熱<br>合計 (kcal) | 小尖端<br>合計 (kcal)         | 使用<br>ルーブ        | 熱成<br>温度 (°C) | 熱成<br>時間 (hr) | 枚数          | 板上熱合<br>の平均ア<br>スペクト<br>比 | 板上熱合<br>の平均ア<br>スペクト<br>比の平均<br>値 (kcal) | 開放気孔<br>の平均<br>孔径 (mm) | 開放気孔<br>率 (%) | アスペクト<br>比 2~50 の<br>板上熱合の<br>合計率 (%) | 熱脱脂子<br>材の熱合<br>率 (kg/kg) | 熱脱脂去<br>除のハニ<br>カム温度<br>(°C) |
| 実<br>験<br>01 | 1<br>初期<br>成形 | 8                 | 0.3              | △孔径<br>20.3<br>出力熱<br>フロ | 2130             | 4             | a             | 4           | 20                        | 8  | 48                     | 80            | 0.4                                   | 1020                      |                              |
|              |               |                   |                  |                          |                  |               | b             | 3.5         | 28                        | 12                                       | 48                     | 83            | 0.5                                   | 1010                      |                              |
|              |               |                   |                  |                          |                  |               | c             | 3.2         | 43                        | 15                                       | 45                     | 85            | 0.6                                   | 1000                      |                              |
|              | 2<br>初期<br>成形 | 8                 | 0.3              | " "                      | 2150             | 4             | a             | 8           | 4                         | 3  | 42                     | 95            | 0.3                                   | 1050                      |                              |
|              |               |                   |                  |                          |                  |               | b             | 4           | 13                        | 8  | 43                     | 90            | 0.5                                   | 1080                      |                              |
|              |               |                   |                  |                          |                  |               | c             | 3.4         | 40                        | 14                                       | 44                     | 87            | 0.6                                   | 1100                      |                              |
|              | 3<br>初期<br>成形 | 8                 | 0.03             | 0.1                      | "                | 2150          | 4             | a           | 8                         | 9  | 4                      | 40            | 98                                    | 0.5                       | 1100                         |
|              |               |                   |                  |                          |                  |               | b             | 8           | 12                        | 9  | 40                     | 98            | 0.6                                   | 1140                      |                              |
|              |               |                   |                  |                          |                  |               | c             | 4           | 28                        | 12                                       | 42                     | 92            | 0.8                                   | 1150                      |                              |
|              | 4<br>初期<br>成形 | 8                 | 0.3              | "                        | 2300             | 10            | a             | 3.8         | 43                        | 19                                       | 40                     | 92            | 0.4                                   | 1000                      |                              |
|              |               |                   |                  |                          |                  |               | b             | 3.1         | 55                        | 21                                       | 47                     | 90            | 0.5                                   | 1000                      |                              |
|              |               |                   |                  |                          |                  |               | c             | 2.5         | 62                        | 21                                       | 47                     | 90            | 0.7                                   | 980                       |                              |
| 5            | 初期<br>成形      | 8                 | 0.3              | "                        | 2050             | 2             | a             | 0.2         | 11                        | 5  | 48                     | 83            | 0.5                                   | 1030                      |                              |
|              |               |                   |                  |                          |                  |               | b             | 3.5         | 19                        | 8  | 48                     | 80            | 0.8                                   | 1080                      |                              |
|              |               |                   |                  |                          |                  |               | c             | 2.5         | 22                        | 9  | 49                     | 85            | 0.9                                   | 1080                      |                              |

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Key: 1 Additives in honeycomb molded body  
2 Additive  
3 Content at periphery (%)  
4 Content at center (%)  
5 Honeycomb molded body sintering conditions  
6 Crucible used  
7 Sintering temperature (°C)  
8 Retention time (h)  
9 Honeycomb structure barrier wall structure  
10 Location  
11 Average aspect ratio of tabular crystals  
12 Average minor diameter thickness of tabular crystals (μm)

- 13 Average pore diameter of open pores ( $\mu\text{m}$ )
- 14 Open porosity (% TD)
- 15 Content of tabular crystals with aspect ratios of 2 to 50 (%)
- 16 Cumulative thickness of trapped particles (mm/5 h)
- 17 Honeycomb temperature at sintering and removal ( $^{\circ}\text{C}$ )
- 18 Application Example
- 19 Free carbon
- 20 Porosity 20%
- Graphite crucible
- Break down
- 21 Properties

As is clear from the table, the honeycomb structure of the present invention has an average pore diameter that progressively increases from the center barrier walls to the peripheral barrier walls. Moreover, when this structure was used for trapping microparticles in exhaust gas for 5 h in the form of a particulate trap filter for diesel engines producing particle diameters of 1 to 30  $\mu\text{m}$ , the thickness of accumulated microparticles changed continuously from the central regions to the peripheral regions in both application examples, with the microparticle thickness being 0.4 mm in the center region (a) and 0.6 mm at the outermost peripheral region (c) in Application Example 1. /7

Consequently, when an excess of  $\text{O}_2$  was added to the honeycomb structure pertaining to the present invention and ignition was brought about at 800 $^{\circ}\text{C}$ , the temperature during temperature elevation was 1000 $^{\circ}\text{C}$  at the periphery in Application Example 1, and the temperature during temperature elevation was 1020 $^{\circ}\text{C}$  at the center. The temperature differential was extremely small in each of the application examples, and there were no problems with fusion damage or resistance to thermal impact.

#### Effect of the invention

The silicon carbide honeycomb structure of the present invention has a three-dimensional network structure in which tabular crystals are intertwined in a complicated manner. Consequently, the structure is effective in heat transfer, chemical reactions, material transfer, and other functions arising at the barrier wall surfaces. In addition, the average pore diameter increases from the center barrier walls to the peripheral barrier walls of the structure, and so the heat of combustion does not accumulate in the center region when heated with the objective of reuse, thereby preventing and fusion damage and thermal shock damage in the barrier walls.

Brief description of the figures

Figure 1 is a plan view of the honeycomb structure of the present invention. Figure 2 is a cross-sectional schematic diagram.

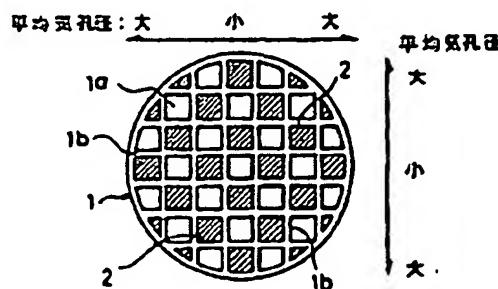


Figure 1

Key:

- 1 Average pore diameter
- 2 Large
- 3 Average pore diameter
- 4 Large
- 5 Small
- 6 Large
- 7 Small
- 8 Large

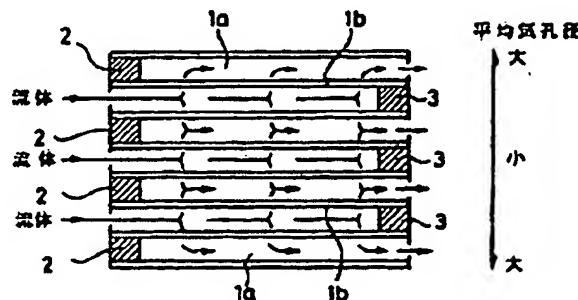


Figure 2

Key:

- 1 Average pore diameter
- 2 Fluid
- 3 large
- 4 Small
- 5 Large